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(21) International Application Number: PCT/US95/01402 (22) International Filing Date: 31 January 1995 (31.01.95) (30) Priority Data: 193,352 8 February 1994 (08.02.94) US 270,695 5 July 1994 (05.07.94) US (71) Applicant: CHEVRON U.S.A. INC. [US/US]; P.O. Box 7141, San Francisco, CA 94120-7141 (US). (72) Inventor: NAKAGAWA, Yumi; 6435 Swainland Road, Oak- land, CA 94611 (US). (74) Agents: SHERIDAN, Richard, J. et al.; Chevron Corporation, Law Dept., San Francisco, CA 94120-7141 (US).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>With international search report.</i>
(54) Title: METHOD FOR PREPARING CRYSTALLINE ALUMINOPHOSPHATE MATERIALS USING AZA-POLYCYCLIC TEM- PLATING AGENTS (57) Abstract Molecular sieves, particularly metalloaluminophosphates are prepared using templates derived from a 4-azonia- tricyclo[5.2.n.o ^{2.6}]alkene family of compounds. The templates may be prepared in a series of reaction steps which include a Diels-Alder reaction between a diene and a dienophile.		

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01 METHOD FOR PREPARING CRYSTALLINE ALUMINOPHOSPHATE MATERIALS
02 USING AZA-POLYCYCLIC TEMPLATING AGENTS
03

04 BACKGROUND OF THE INVENTION
05

06 Field of the Invention
07

08 The present invention relates to a new method for
09 synthesizing crystalline molecular sieves using a family of
10 templating agents.
11

12 Background
13

14 The crystalline materials of this invention contain metallic
15 and non-metallic oxides bonded through oxygen linkages to
16 form a three-dimensional structure. Molecular sieves are a
17 commercially important class of crystalline materials.
18 Natural and synthetic crystalline molecular sieves are
19 useful as catalysts and adsorbents. They have distinct
20 crystal structures with ordered pore structures which are
21 demonstrated by distinct X-ray diffraction patterns. The
22 crystal structure defines cavities and pores which are
23 characteristic of the different species. The adsorptive and
24 catalytic properties of each molecular sieve are determined
25 in part by the dimensions of its pores and cavities. Thus,
26 the utility of a particular molecular sieve in a particular
27 application depends at least partly on its crystal
28 structure.
29

30 Because of their unique sieving characteristics, as well as
31 their catalytic properties, molecular sieves are especially
32 useful in such applications as gas drying and separation and
33 hydrocarbon conversion. Although many different molecular
34 sieves have been disclosed, there is a continuing need for

-2-

01 new materials with desirable properties for gas separation
02 and drying, hydrocarbon and chemical conversions, and other
03 applications.
04
05 Aluminophosphate molecular sieves containing $[AlO_2]$ and $[PO_2]$
06 units have been disclosed in U.S. Patent No. 4,310,440,
07 issued January 12, 1982 to Wilson et al.
08 Silicoaluminophosphates having a three-dimensional crystal
09 framework of PO_2^+ , AlO_2^- and SiO_2 tetrahedral units are taught
10 in U.S. Patent No. 4,440,871, issued April 3, 1984 to Lok
11 et al. Aluminophosphates containing $[AlO_2]$ and $[PO_2]$
12 structural units, and one or more metals in tetrahedral
13 coordination with oxygen atoms are disclosed in U.S. Patent
14 No. 4,567,029, issued January 28, 1986 to Wilson et al. The
15 '029 reference teaches using the metals magnesium,
16 manganese, zinc, and cobalt, and uses the nomenclature
17 "MeAPO" to identify these metal aluminophosphate materials.
18 U.S. Patent No. 4,686,093, issued August 11, 1987 to
19 Flanigen et al., describes aluminophosphates containing at
20 least two elements selected from arsenic, beryllium, boron,
21 chromium, gallium, germanium, lithium and vanadium. U.S.
22 Patent No. 4,913,799, issued April 3, 1990 to Gortsema
23 et al., discloses a large number of aluminophosphates for
24 use in hydrocracking processes. The aluminophosphates of
25 '799 contain $[AlO_2]$ and $[PO_2]$ structural units, and one or
26 more metals in tetrahedral coordination, including arsenic,
27 beryllium, boron, chromium, cobalt, gallium, germanium,
28 iron, lithium, magnesium, manganese, silicon, titanium,
29 vanadium, and zinc. U.S. Patent No. 4,973,785, issued
30 November 27, 1990 to Lok et al., expands the list of
31 aluminophosphates, and teaches the use for converting
32 hydrocarbons using silicoaluminophosphates containing at
33 least one element, "EL" capable of forming a three
34

-3-

01 dimensional oxide framework having a mean "EL---O" distance
02 in tetrahedral oxide structures between 1.51Å and 2.06Å,
03 where "EL" has a cation electronegativity between 125 to 310
04 kcal/g-atom, and is capable of forming stable EL--O--P,
05 EL--O--Al or El--O--El bonds in crystalline three
06 dimensional oxide structures having an "EL--O" bond
07 dissociation energy greater than about 59 kcal/mole at
08 289°C.

09

10 Organic templating agents are believed to play an important
11 role in the process of molecular sieve crystallization.
12 Organic amines and quaternary ammonium cations were first
13 used in the synthesis of zeolites in the early 1960's. This
14 approach led to a significant increase in the number of new
15 zeolitic structures discovered as well as an expansion in
16 the boundaries of composition of the resultant crystalline
17 products.

18

19 Unfortunately, the relationship between structure of the
20 organocation and the resultant zeolite is far from
21 predictable, as evidenced by the multitude of products which
22 can be obtained using a single quaternary ammonium salt as
23 reported by S. I. Zones et al., 1989, *Zeolites: Facts,*
24 *Figures, Future*, ed. P. A. Jacobs and R. A. van Santen,
25 pp. 299-309, Amsterdam: Elsevier Science Publishers., or the
26 multitude of organocations which can produce a single
27 zeolitic product as reported by R. M. Barrer, 1989, *Zeolite*
28 *Synthesis*, ACS Symposium 398, ed. M. L. Occelli and H. E.
29 Robson, pp. 11-27, American Chemical Society.

30

31 Thus, it is known that organocations exert influence on the
32 molecular sieve crystallization processes in many
33 unpredictable ways. Aside from acting in a templating role,
34 the organic cation's presence also greatly affects the

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01 characteristics of the gel. These effects can range from
02 modifying the gel pH to altering the interactions of the
03 various components via changes in hydration (and thus
04 solubilities of reagents) and other physical properties of
05 the gel. Accordingly, investigators have now begun to
06 consider how the presence of a particular quaternary
07 ammonium salt influences many of these gel characteristics
08 in order to determine more rigorously how such salts exert
09 their templating effects.

10
11 It has been noted that many of the organocations which have
12 been used as templates for zeolite synthesis are
13 conformationally flexible. These molecules can adopt many
14 conformations in aqueous solution, therefore several
15 templates can give rise to a particular crystalline product.
16 Studies which involved alterations on such conformationally
17 flexible organic amines and cations have been published.
18 For example, one study, Rollmann and Valyocsik, 1985,
19 *Zeolites* 5, 123, describes how varying the chain length for
20 a series of α,ω -linear diamines resulted in different
21 intermediate-pore products. It has also been recently
22 reported by M. D. Shannon et al., 1991, *Nature* 353, 417-420
23 and J. L. Casci, 1986, *New Developments in Zeolite Science*
24 *and Technology*, ed. Y. Murakami et al., pp. 215-222,
25 Elsevier that three different products which have related
26 framework topologies, can be formed from three linear
27 bis-quaternary ammonium templates of varying chain lengths.

28
29 Altering the structure of a conformationally rigid organic
30 molecule can also lead to a change in the zeolite obtained,
31 presumably due to the differing steric demands of each
32 template. S. I. Zones, 1989, *Zeolites* 9, 458-467 reported
33 that in switching from 1,3-dimethylimidazolium hydroxide to
34 1,3-diisopropylimidazolium hydroxide as template, using the

-5-

01 same starting gel ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$), the former directs
02 toward formation of ZSM-22 whereas the latter affords
03 ZSM-23.

04

05 In summary, a variety of templates have been used to
06 synthesize a variety of molecular sieves, including
07 zeolites, aluminophosphates, and silicoaluminophosphates.
08 Though the specific utility of a given template is at
09 present unpredictable, a few notable cyclic-organocation
10 templating agents have been reported. For instance, use of
11 N,N,N-trimethyl cyclopentylammonium iodide in the
12 preparation of Zeolite SSZ-15 molecular sieve is disclosed
13 in U.S. Patent No. 4,610,854, issued September 9, 1986 to
14 Zones; use of 1-azoniaspiro [4.4] nonyl bromide and
15 preparation of a molecular sieve termed "Losod" is disclosed
16 in *Hel. Chim. Acta* (1974), Vol. 57, page 1533 (W. Sieber and
17 W. M. Meier); use of 1, ω -di(1-azoniabicyclo [2.2.2.] octane)
18 lower alkyl compounds in the preparation of Zeolite SSZ-16
19 molecular sieve is disclosed in U.S. Patent No. 4,508,837,
20 issued April 2, 1985 to Zones; use of N,N,N-trialkyl-1
21 adamantammonium salts in the preparation of zeolite SSZ-13
22 molecular sieve is disclosed in U.S. Patent No. 4,544,538,
23 issued October 1, 1985 to Zones. U.S. Patent No. 5,053,373,
24 issued October 1, 1991 to Zones discloses preparing SSZ-32
25 with an N-lower alkyl-N'-isopropyl-imidazolium cation
26 templating agent. U.S. Patent No. 5,106,801, issued April
27 21, 1992 to Zones et al. discloses a cyclic quaternary
28 ammonium ion, and specifically a tricyclodecane quaternary
29 ammonium ion, for the preparation of the metallocate
30 zeolite SSZ-31. U.S. Patent No. 4,910,006, issued March 20,
31 1990 to Zones et al., teaches using a
32 hexamethyl[4.3.3.0]propellane-8,11-diammonium cation for the
33 preparation of SSZ-26. EP 0193282 discloses a tropinium
34 cation for preparing the clathrasil ZSM-58. Similarly, use

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01 of quinuclidinium compounds to prepare a zeolite termed
02 "NU-3" is disclosed in European Patent Publication
03 No. 40016.

04

05 The use of 1,4-diazabicyclo[2,2,2]octane; N,N'-dimethyl-1,4
06 diazabicyclo[2,2,2]octane dihydroxide; and quinuclidine are
07 examples of amines taught in U.S. Patent No. 4,310,440,
08 issued January 12, 1982 to Wilson et al., and U.S. Patent
09 No. 4,440,871, issued April 3, 1984 to Lok et al. for the
10 preparation of aluminophosphates and silicoaluminophosphates
11 respectively.

12

13

SUMMARY OF THE INVENTION

14

15 This invention provides a novel process for preparing
16 crystalline materials, particularly molecular sieves having
17 framework structures comprising $[\text{AlO}_2]$ and $[\text{PO}_2]$ units. This
18 process includes contacting active sources of the components
19 of the crystalline materials with an organocationic
20 templating agent which is derived from a
21 4-azonia-tricyclo[5.2.n.0^{2.6}]alkene family of compounds,
22 wherein each member of the family is a compound which may be
23 prepared via a Diels-Alder reaction pathway.

24

25 More specifically, a method is provided for preparing a
26 crystalline molecular sieve comprising oxides of one or more
27 trivalent element(s) and oxides of one or more pentavalent
28 element(s), said method comprising contacting under
29 crystallization conditions one or more active sources of
30 said oxides with a templating agent having a molecular
31 structure of the form:

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-7-

01 (I)

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12 (IA)

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16

17 wherein:

18

19 R1 and R2 are at each independent occurrence selected
 20 from the group consisting of hydrogen, a lower alkyl
 21 group, and when taken together, a spirocyclic group
 22 having from 3 to 6 carbon atoms;

23

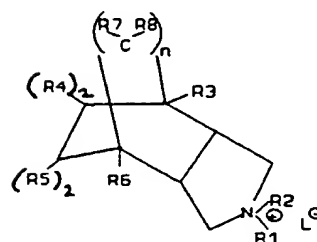
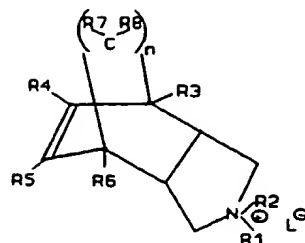
24 R3, R4, R5 and R6 are at each independent occurrence
 25 selected from the group consisting of hydrogen,
 26 halogen, and a lower alkyl group;

27

28 n has at each independent occurrence a value of 1, 2,
 29 3, or 4;

30

31 R7 and R8 are at each independent occurrence selected
 32 from the group consisting of hydrogen and a lower alkyl
 33 group, and when n is one (1), R7 and R8 can be taken
 34 together to form a spirocyclic group having from 3 to 6

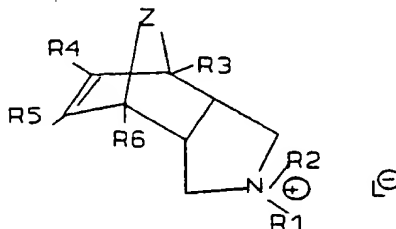


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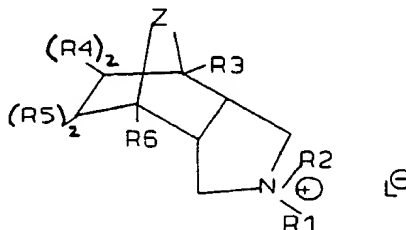
carbon atoms; and when n is two (2) or greater, one of R7 and R8 on one carbon atom can be taken together with one of R7 and R8 on an adjacent carbon atom to form a ring having from 3 to 6 carbon atoms; and

L is an anion which is not detrimental to the formation of the molecular sieve, such as anions including halogens, such as fluoride, chloride, bromide, and iodide, hydroxide, acetate, sulfate, carboxylate, with hydroxide being most preferred, or a molecular structure of the form:

(II)



(IIA)



wherein:

Z is at each independent occurrence selected from the group consisting of oxygen, nitrogen, sulfur, and a hydrocarbyl (e.g., alkylene, alkylidene, substituted

-9-

01 alkylene and the like having 1 to about 6 carbon atoms)
02 radical; and

03

04 R1, R2, R3, R4, R5, R6, and L are as defined above.

05

06 Aza-polycyclic compounds encompassed by this formula are
07 hereinafter referred to as the "defined aza-polycyclic
08 templating agents".

09

10 The molecular sieve of this invention has a three-
11 dimensional microporous framework structure comprising
12 [AlO₂] and [PO₂] oxide units. The molecular sieve may
13 additionally comprise an oxide of at least one element other
14 than aluminum and phosphorous which is capable of forming an
15 oxide in tetrahedral coordination with [AlO₂] and [PO₂] oxide
16 structural units in the molecular sieve. The preferred
17 elements other than aluminum and phosphorous are selected
18 from the group consisting of arsenic, beryllium, boron,
19 chromium, cobalt, gallium, germanium, iron, lithium,
20 magnesium, manganese, silicon, titanium, vanadium, and zinc.
21 Silicon, magnesium, manganese, cobalt, and zinc are more
22 preferred, with silicon being particularly preferred.

23

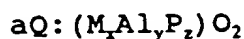
24 The present invention is also directed to a crystalline
25 molecular sieve comprising oxides of one or more trivalent
26 element(s) and of one or more pentavalent element(s), and
27 having therein the defined aza-polycyclic templating agent.

28

29 Preferably, the molecular sieve has a molar composition, as
30 synthesized and in the anhydrous state, as follows:

31

32



33

34 wherein:

-10-

01 Q is the defined aza-polycyclic templating agent having
02 a molecular structure of the form shown in Structure I,
03 IA, II or IIA above;

04

05 a has a value in the range of greater than zero and no
06 greater than about 0.3;

07

08 M is one or more elements capable of forming stable
09 M--O--P, M--O--Al, or M--O--M bonds in crystalline
10 oxide structures;

11

12 y and z each have a value of at least 0.01; and

13

14 the sum of x, y, and z is 1.

15

16 Among other factors, the present invention is based on the
17 discovery that small changes in structure within this family
18 of relatively rigid, polycyclic templating agents, when the
19 template is used in molecular sieve synthesis, can lead to
20 significant changes in the crystalline molecular sieve
21 formed.

22

23 DETAILED DESCRIPTION OF THE INVENTION

24

25 In preparing a crystalline material according to the present
26 invention, a defined aza-polycyclic compound, having a
27 general molecular structure of the form shown in Structure I
28 above, acts as a template or structure directing agent
29 during the crystallization. Typically, the defined
30 aza-polycyclic templating agent is prepared in a series of
31 reaction steps comprising a Diels-Alder reaction between a
32 diene and a dienophile.

33

34

-11-

01 In another embodiment is the molecular sieve, in its
02 as-synthesized form containing the defined aza-polycyclic
03 templating agent.

04

05 In the method of this invention the family of aza-polycyclic
06 cations can be used to synthesize different aluminophosphate
07 materials depending on the reagents, reactant ratios and
08 reaction conditions. For example, factors which may affect
09 the crystallization of a given aluminophosphate include the
10 specific defined aza-polycyclic template used, the type and
11 ratio of inorganic reagents used, the methods used in mixing
12 reagents and the temperature and time used in
13 crystallization.

14

15 The full scope of the composition and process of the present
16 invention will be apparent to those familiar with
17 crystalline molecular sieves and their methods of
18 preparation from the following detailed description of the
19 principal features of the composition and from the examples
20 which accompany the description.

21

22

The Templating Agent

23

24 The templating agents useful in the present process are
25 derived from the 4-azonia-tricyclo[5.2.n.0^{2,6}]alkene family
26 of compounds, where n is a number and has a value of 1, 2,
27 3, or 4. The templating agent has a molecular structure of
28 the general form:

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-12-

01 (I)

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12 (IA)

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16

17 wherein R1, R2, R3, R4, R5, R6, R7, R8, L and n are as
18 defined above.

19

20 The templating agent may also have a molecular structure of
21 the general form:

22

23

24

25 (II)

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29

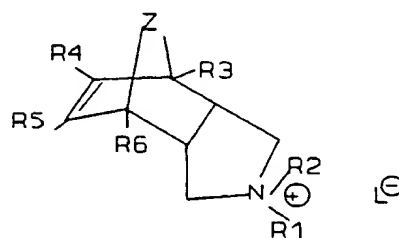
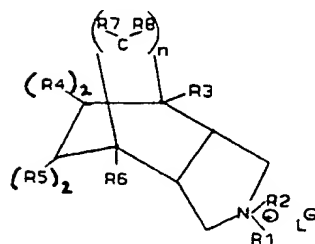
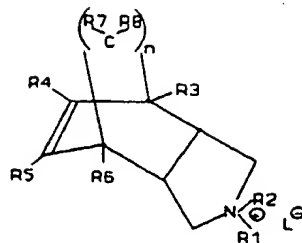
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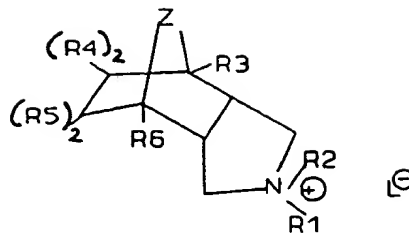
33

34



-13-

(IIA)



wherein R1, R2, R3, R4, R5, R6, Z and L are as defined above.

Preferably, R1 and R2 are each selected from the group consisting of hydrogen, an alkyl group having from 1 to 3 carbon atoms, and when taken together, a spirocyclic group having from 3 to 6, more preferably from 4 to 5, carbon atoms.

Preferably, R3, R4, R5 and R6 are each selected from the group consisting of hydrogen, halogen, and an alkyl group having from 1 to 3 carbon atoms.

Preferably, R7 and R8 are each selected from the group consisting of hydrogen and an alkyl group having from 1 to 3 carbon atoms, and when n is one (1), R7 and R8 can be taken together to form a spirocyclic group having from 3 to 6, more preferably from 3 to 5, carbon atoms; and when n is two (2) or greater, one of R7 and R8 on one carbon atom can be taken together with one of R7 and R8 on an adjacent carbon atom to form a ring having from 3 to 6, more preferably from 3 to 5, carbon atoms.

As used herein, the term "halogen" refers to fluorine, chlorine, bromine, iodine and combinations thereof. The term "lower alkyl group" refers to a linear, branched, or cyclic alkyl group having from 1 to 6 carbon atoms. The

-14-

01 term "spirocyclic group" refers to a cyclic group in a
02 polycyclic hydrocarbon having one carbon atom in common with
03 a second cyclic group. L is an anion which is not
04 detrimental to the formation of the molecular sieve.
05 Representative anions include halogens, such as fluoride,
06 chloride, bromide, and iodide, hydroxide, acetate, sulfate,
07 carboxylate. Hydroxide is the most preferred anion. It may
08 be beneficial to ion exchange, for example, the halide for
09 hydroxide ion, thereby reducing or eliminating the alkali
10 metal hydroxide quantity required.

11

12 Many of the organocations which have been previously used as
13 templates for molecular sieve synthesis are conformationally
14 flexible. These molecules adopt many conformations in
15 aqueous solution, and several templates can give rise to a
16 single crystalline product. In contrast, the defined
17 aza-polycyclic templating agents used in the present
18 invention are conformationally rigid organic molecules.
19 Altering the structure of these rigid molecules can lead to
20 a change in the molecular sieve obtained, presumably due to
21 the differing steric demands of each template. In
22 particular, it has been found that the present templating
23 agents are useful for synthesizing large pore molecular
24 sieves, which are important for certain catalytic
25 applications.

26

27 Increasing the steric demand of the template may lead to a
28 decrease in crystallization rate as well as a decrease in
29 template solubility in the reaction mixture. If the
30 template is not sufficiently soluble, it will be difficult
31 to form crystals in the reaction mixture. Addition of a
32 surfactant to the reaction mixture may help to solubilize
33 the template.

34

-15-

01 Employing a Diels-Alder reaction scheme, using inexpensive
02 reagents, is the preferred method for preparing the present
03 templating agents. The Diels-Alder reaction is one of the
04 most useful transformations in synthetic organic chemistry.
05 Two new bonds and a six-membered ring are formed in the
06 Diels-Alder reaction, formally a [4+2]cycloaddition of a
07 1,4-conjugated diene with a double bond (dienophile). The
08 dienophile may include a carbon-carbon, carbon-heteroatom,
09 or heteroatom-heteroatom double (or triple) bond, leading to
10 a diverse pool of potential templating agents. Electron-
11 withdrawing groups on the dienophile greatly increase its
12 reactivity, whereas electron-donating groups on the diene
13 have the same effect. The Diels-Alder reaction is discussed
14 in greater detail in F. Fringuelli and A. Taticchi, *Dienes*
15 *in the Diels-Alder Reaction 1990*, J. Wiley and Sons, Inc.

16

17 The versatility of the Diels-Alder reaction is in part
18 responsible for its usefulness. A wide range of starting
19 materials are available, making possible the preparation of
20 numerous products. The stereoelectronics of the reaction,
21 as well as its concerted nature, often allows one to predict
22 which product will be formed if several are possible.
23 Therefore, by the proper choice of starting materials, very
24 efficient syntheses of target templates can be achieved.

25

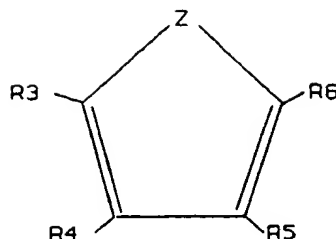
26 In particular, the Diels-Alder reaction pathway provides a
27 method for synthesizing the defined aza-polycyclic ring
28 systems which are useful in the present process. Varying
29 either the diene or the dienophile produces small but
30 significant structural changes to the key intermediates in
31 the synthesis.

32

33 The dienes useful for preparing the defined aza-polycyclic
34 templates are of the following general form:

-16-

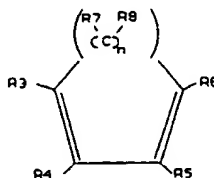
(III)



wherein R3, R4, R5, R6, and Z are as defined above.

In a further embodiment, the dienes useful for preparing the defined aza-polycyclic templates have the following form:

(IV)



wherein R3, R4, R5, R6, R7, R8, and n are as defined above.

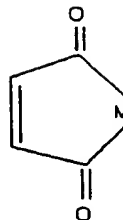
Examples of cyclic dienes having a carbon backbone include cyclopentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, 1,3-cycloheptatriene, spiro[2,4]hepta-4,6-diene, and 1,3-cyclooctadiene. The diene of Structure III may also include one or more heteroatoms in the cyclic backbone, including oxygen, nitrogen, and/or sulfur. Oxygen is preferred. Non-limiting examples of heterodienes which are used in preparing the templating agent include furan, pyrrol, and thiophene. Examples of functional groups R7 and R8 in Structure IV are hydrogen, methyl, ethyl, propyl, and cyclopropyl.

The dienophile from which the present templating agent is prepared has a structure of the general form:

-17-

01
02
03
04
05
06
07

(V)



08 wherein X is either oxygen or nitrogen having a substituent
09 group selected from the group consisting of hydrogen and a
10 lower alkyl group.

11

12 The defined aza-polycyclic compounds are prepared by methods
13 known in the art. The reactions involved are described in
14 detail in, for example, *Chem. Pharm. Bull.* (1962), 10,
15 714-718, L. F. Fieser and M. Fieser, 1967, *Reagents for*
16 *Organic Synthesis*, vol 1, pp. 581-594, New York: J. Wiley
17 and Sons, Inc. and W. K. Anderson and A. S. Milowsky, 1985,
18 *J. Org. Chem.* 50,5423-24. When a diene, such as that shown
19 in Structure IV above, is reacted with a dienophile such as
20 that shown in Structure V, element M is oxygen, the
21 resulting product is reacted with an amine to form an imide,
22 then reduced to the corresponding pyrrolidine using a
23 reducing agent such as lithium aluminum hydride, and then
24 quaternized with, for example methyl iodide, to form the
25 defined aza-polycyclic templating agent.

26

27 When the diene of Structure III or IV above, is reacted with
28 a dienophile of Structure V, wherein element M is nitrogen
29 having a lower alkyl substituent group, the resulting imide
30 product is directly reduced to the corresponding pyrrolidine
31 and then quaternized to form the cationic templating agent.

32

33 The double bond shown in Structures I and II above is not
34 critical to the action of the defined aza-polycyclic

-18-

01 compound as a templating agent, and may be reduced, using
02 techniques readily available in the art, such as, for
03 example, by reaction over a palladium/carbon or a
04 platinum/carbon catalyst in the presence of hydrogen. The
05 reduced compound will also serve as a templating agent in
06 the present method.

07

08

The Reaction Mixture

09

10 The molecular sieves of this invention can be prepared from
11 an aqueous solution comprising sources of one or more
12 trivalent elements, one or more pentavalent elements and the
13 defined aza-polycyclic templating agents of this invention.
14 Typically, the trivalent element will be aluminum and the
15 pentavalent element will be phosphorus. The reaction
16 mixture may optionally can sources of another element(s) (M)
17 capable of forming stable M--O--P, M--O--Al or M--O--P bonds
18 in the molecular sieve crystalline oxide structure.

19

20 In general, the reaction mixture should have a composition,
21 in terms of mole ratios of oxides, within the ranges shown
22 below. For convenience, aluminum has been used as the
23 trivalent element and phosphorus as the pentavalent element,
24 but it is not intended that the tri- and pentavalent
25 elements be limited to those elements.

26

27 $\text{Al}_2\text{O}_3 : \text{P}_2\text{O}_5 : 0-0.2 \text{ MO}_2 : 0.5 \text{ Q}_2\text{O} : 120-140 \text{ H}_2\text{O}$

28

29 where M is the element (typically silicon) capable of
30 forming the stable M--O--Al, M--O--P or M--O--M bonds, and Q
31 is the defined aza-polycyclic templating agent.

32

33

34

-19-

01 Crystalline Materials of this Invention

02

03 The crystalline material of this invention comprises the
04 defined aza-polycyclic templating agent in combination with
05 one or more metallic and/or non-metallic oxides bonded in
06 tetrahedral coordination through shared oxygen atoms to form
07 a cross-linked three dimensional crystal structure. The
08 metallic and non-metallic oxides comprise one or more
09 trivalent element(s) and one or more pentavalent element(s).
10 The trivalent element is preferably aluminum and the
11 pentavalent element is preferably phosphorous. The entire
12 lattice is charge balanced.

13

14 The term "molecular sieve" refers to a material prepared
15 according to the present invention having a fixed,
16 open-network structure, usually crystalline, that may be
17 used to separate hydrocarbons or other mixtures by selective
18 occlusion of one or more of the constituents, or may be used
19 as a catalyst in a catalytic conversion process.

20

21 The term "metalloaluminophosphate" encompasses crystalline
22 molecular sieves comprising tetrahedrally-bound $[AlO_2]$ and
23 $[PO_2]$ oxide structural units. Examples include crystalline
24 aluminophosphates having a chemical composition, in oxide
25 mole ratios, of $Al_2O_3:1.0 \pm 0.2 P_2O_5$. Optionally, the
26 crystalline metalloaluminophosphate may further comprise, in
27 addition to aluminum and phosphorous, tetrahedrally-bound
28 oxide units of one or more elements which are capable of
29 forming tetrahedral oxide units with the $[AlO_2]$ and $[PO_2]$
30 units, including arsenic, beryllium, boron, chromium,
31 cobalt, gallium, germanium, iron, lithium, magnesium,
32 manganese, silicon, titanium, vanadium, and zinc.

33

34

-20-

01 Typically, the crystalline material has a molar composition,
02 as synthesized and in the anhydrous state, as follows:

03

04



05

06 wherein:

07

08 Q is the defined aza-polycyclic templating agent having
09 a molecular structure of the form shown in Structure I,
10 IA, II or IIA above;

11

12 a has a value in the range of greater than zero and no
13 greater than about 0.3;

14

15 M is one or more elements capable of forming stable
16 M--O--P, M--O--Al, or M--O--M bonds in crystalline
17 oxide structures;

18

19 y and z each have a value of at least 0.01; and

20

21 the sum of x, y, and z is 1.

22

23 The crystalline material can be suitably prepared from an
24 aqueous solution containing at least one defined
25 aza-polycyclic templating agent, and sources of at least one
26 oxide capable of forming a crystalline molecular sieve.
27 Examples of a suitable metal oxide include an alkali metal
28 oxide, and oxides of aluminum, silicon, boron, germanium,
29 iron, gallium, phosphorous, arsenic, beryllium, chromium,
30 cobalt, gallium, magnesium, manganese, titanium, vanadium,
31 and zinc.

32

33 The present process is suitable for preparing a
34 metalloaluminophosphate molecular sieve from a reaction

-21-

01 mixture prepared using standard preparation techniques.
02 Aluminophosphates and the conventional preparation thereof
03 are described in U.S. Patent No. 4,310,440, issued
04 January 12, 1982 to Wilson et al., the disclosure of which
05 is incorporated herein by reference.
06 Silicoaluminophosphates and the conventional preparation
07 thereof are described in U.S. Patent No. 4,440,871, issued
08 April 3, 1984 to Lok et al., and U.S. Patent No. 4,943,424,
09 issued July 24, 1990 to Miller, the disclosures of which are
10 incorporated herein by reference. Metalloaluminophosphates
11 and the convention preparation thereof are described in U.S.
12 Patent No. 4,913,799, issued April 30, 1990 to Gortsema
13 et al., the disclosure of which is incorporated by
14 reference. In the '799 patent the metalloaluminophosphates
15 are termed "non-zeolitic molecular sieve".
16
17 The preferred source of aluminum for the crystalline
18 aluminophosphate and metal aluminophosphate molecular sieves
19 of this invention is an aluminum alkoxide such as aluminum
20 isopropoxide or pseudo-boehmite. Phosphoric acid is the
21 preferred source of phosphorous. Organic phosphates and
22 crystalline aluminophosphates can also be employed as a
23 source of phosphorous. Typical sources of silicon oxide
24 include silicates, silica hydrogel, silicic acid, colloidal
25 silica, tetra-alkyl orthosilicates, and silica hydroxides.
26 Sources of the other oxides typically include salts which
27 are soluble in the reaction mixture.
28
29 In preparing the crystalline material under crystallization
30 conditions according to the present invention, the reaction
31 mixture is maintained under hydrothermal conditions at an
32 elevated temperature until crystals are formed. The
33 temperatures during the hydrothermal crystallization step
34 are typically maintained from about 50°C to about 200°C.

-22-

01 The crystallization period is typically greater than 1 day
02 and preferably from about 3 days to about 50 days.

03

04 The hydrothermal crystallization is usually conducted under
05 pressure and usually in an autoclave so that the reaction
06 mixture is subject to autogenous pressure. The reaction
07 mixture can be stirred during crystallization.

08

09 More specifically, the synthesis method for preparing
10 metalloaluminophosphates comprises:

11

12 (a) preparing an aqueous reaction mixture containing
13 aluminum isopropoxide and phosphoric acid,
14 thereafter combining the aqueous reaction mixture
15 with an organic templating agent and optionally
16 adding active source(s) of one or more additional
17 elements capable of forming oxides in tetrahedral
18 coordination with $[AlO_2]$ and $[PO_2]$ units, to form
19 the complete reaction mixture in the relationship
20 herein before set forth;

21

22 (b) heating the complete reaction mixture to a
23 temperature in the range of from 50°C to 240°C and
24 preferably from 100°C to 200°C until crystals are
25 formed, usually from 5 hours to 500 hours and
26 preferably 24 to 480 hours; and

27

28 (c) recovering the crystalline product.

29

30 Once the crystals have formed, the solid product is
31 separated from the reaction mixture by standard mechanical
32 separation techniques, such as filtration. The crystals are
33 water-washed and then dried, e.g., at 90°C to 150°C for from
34 8 to 24 hours, to obtain the synthesized zeolite crystals.

-23-

01 The drying step can be performed at atmospheric or
02 subatmospheric pressures.

03

04 During the hydrothermal crystallization step, the crystals
05 can be allowed to nucleate spontaneously from the reaction
06 mixture. The reaction mixture can also be seeded with
07 crystals both to direct, and accelerate the crystallization,
08 as well as to minimize the formation of undesired
09 contaminants. If the reaction mixture is seeded with
10 crystals, the concentration of the defined aza-polycyclic
11 template may sometimes be somewhat reduced.

12

13 Due to the unpredictability of the factors which control
14 nucleation and crystallization in the art of crystalline
15 oxide synthesis, not every combination of reagents, reactant
16 ratios, and reaction conditions will result in crystalline
17 products. Selecting crystallization conditions which are
18 effective for producing crystals may require routine
19 modifications to the reaction mixture composition or to the
20 reaction conditions, such as temperature and/or
21 crystallization time. Making these modifications are well
22 within the capabilities of one skilled in the art.

23

24 The crystalline material can be thermally treated
25 (calcined). Usually, it is desirable to remove the alkali
26 metal cation by ion exchange and replace it with hydrogen,
27 ammonium, or any desired metal ion. The molecular sieve can
28 be leached with chelating agents, e.g., EDTA or dilute acid
29 solutions, to increase the silica/alumina mole ratio. The
30 molecular sieve can also be steamed; steaming helps
31 stabilize the crystalline lattice to attack from acids. The
32 molecular sieve can be used in intimate combination with
33 hydrogenating components, such as tungsten, vanadium
34 molybdenum, rhenium, nickel cobalt, chromium, manganese, or

-24-

01 a noble metal, such as palladium or platinum, for those
02 applications in which a hydrogenation-dehydrogenation
03 function is desired. Typical replacing cations can include
04 metal cations, e.g., rare earth, Group IIA and Group VIII
05 metals, as well as their mixtures. Of the replacing
06 metallic cations, cations of metals such as rare earth, Mn,
07 Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are
08 particularly preferred.

09

10 The hydrogen, ammonium, and metal components can be
11 exchanged into the zeolite. The molecular sieve can also be
12 impregnated with the metals, or, the metals can be
13 physically intimately admixed with the molecular sieve using
14 standard methods known to the art. The metals can also be
15 occluded in the crystal lattice by having the desired metals
16 present as ions in the reaction mixture from which the
17 molecular sieve is prepared.

18

19 Typical ion exchange techniques involve contacting the
20 synthetic molecular sieve with a solution containing a salt
21 of the desired replacing cation or cations. Although a wide
22 variety of salts can be employed, chlorides and other
23 halides, nitrates, and sulfates are particularly preferred.
24 Representative ion exchange techniques are disclosed in a
25 wide variety of patents including U.S. Patent
26 Nos. 3,140,249, issued July 7, 1964 to Plank et al.;
27 3,140,251, issued July 7, 1964 to Plank et al.; and
28 3,140,253, issued July 7, 1964 to Plank et al. Ion exchange
29 can take place before or after the zeolite is calcined.

30

31 Following contact with the salt solution of the desired
32 replacing cation, the zeolite is typically washed with water
33 and dried at temperatures ranging from 65°C to about 315°C.
34 After washing, the molecular sieve can be calcined in air or

-25-

01 inert gas at temperatures ranging from about 200°C to about
02 800°C for periods of time ranging from 1 to 48 hours, or
03 more, to produce a catalytically active product especially
04 useful in hydrocarbon conversion processes.

05

06 Regardless of the cations present in the synthesized form of
07 the molecular sieve, the spatial arrangement of the atoms
08 which form the basic crystal lattice of the zeolite remains
09 essentially unchanged. The exchange of cations has little,
10 if any effect on the molecular sieve lattice structures.

11

12 The molecular sieve can be formed into a wide variety of
13 physical shapes. Generally speaking, the molecular sieve
14 can be in the form of a powder, a granule, or a molded
15 product, such as extrudate having a particle size sufficient
16 to pass through a 2-mesh (Tyler) screen and be retained on a
17 400-mesh (Tyler) screen. In cases where the catalyst is
18 molded, such as by extrusion with an organic binder, the
19 aluminosilicate can be extruded before drying, or, dried or
20 partially dried and then extruded.

21

22 The molecular sieve can be composited with other materials
23 resistant to the temperatures and other conditions employed
24 in organic conversion processes. Such matrix materials
25 include active and inactive materials and synthetic or
26 naturally occurring zeolites as well as inorganic materials
27 such as clays, silica and metal oxides. The latter may be
28 naturally occurring or may be in the form of gelatinous
29 precipitates, sols, or gels, including mixtures of silica
30 and metal oxides. Use of an active material in conjunction
31 with the synthetic molecular sieve, combined with it, can
32 improve the conversion and selectivity of the catalyst in
33 certain organic conversion processes. Inactive materials
34 can serve as diluents to control the amount of conversion in

-26-

01 a given process so that products can be formed economically
02 without using other means for controlling the rate of
03 reaction. Frequently, molecular sieve materials have been
04 incorporated into naturally occurring clays, e.g., bentonite
05 and kaolin. These materials, i.e., clays, oxides, etc.,
06 function, in part, as binders for the catalyst. It is
07 desirable to provide a catalyst having good crush strength
08 and attrition resistance, because in petroleum refining the
09 catalyst is often subjected to rough handling. This tends
10 to break the catalyst down into powders which cause problems
11 in processing.

12

13 Naturally occurring clays which can be composited with the
14 synthetic molecular sieves of this invention include the
15 montmorillonite and kaolin families, which families include
16 the sub-bentonites and the kaolins commonly known as Dixie,
17 McNamee, Georgia and Florida clays or others in which the
18 main mineral constituent is halloysite, kaolinite, dickite,
19 nacrite, or anauxite. Various clays such as sepiolite and
20 attapulgite can also be used as supports. Such clays can be
21 used in the raw state as originally mined or can be
22 calcined, treated with acid, or chemically modified.

23

24 In addition to the foregoing materials, the molecular sieve
25 can be composited with porous matrix materials and mixtures
26 of matrix materials such as silica, alumina, titania,
27 magnesia, silica-alumina, silica-magnesia, silica-zirconia,
28 silica-thoria, silica-beryllia, silica-titania, titania-
29 zirconia as well as ternary compositions such as silica-
30 alumina-thoria, silica-alumina-zirconia, silica-alumina-
31 magnesia and silica-magnesia-zirconia. The matrix can be in
32 the form of a cogel.

33

34

-27-

01 The molecular sieve can also be composited with zeolites
02 such as synthetic and natural faujasites (e.g., X and Y),
03 erionites, and mordenites. They can also be composited with
04 purely synthetic zeolites. The combination of molecular
05 sieves and zeolites can also be composited in a porous
06 inorganic matrix.

07

08 The materials prepared in accordance with this invention are
09 useful as molecular sieves, catalysts and/or catalyst
10 carriers.

11

12 The following examples demonstrate but do not limit the
13 present invention.

14

15

EXAMPLES

16

17 Examples 1-11 show that one can make a wide range of
18 templates using the methodology described above. In each of
19 Examples 1-11, the anion L may be either I⁻ or OH⁻.

20

21

Example 1

22

Diels-Alder adduct:

23

24
25 The diene cyclopentadiene was obtained by cracking
26 dicyclopentadiene in a 1-L round bottomed flask fitted with
27 a 30-cm Vigreux column, following the procedure in R. B.
28 Moffett, 1963, *Organic Syntheses Coll. Vol IV*, ed.
29 N. Rabjohn, pp. 238-241, New York: J. Wiley and Sons, Inc.
30 The cyclopentadiene product was distilled from the cracking
31 vessel and recovered. A 2-L, 3-necked flask was equipped
32 with a magnetic stir bar, reflux condenser and thermometer.
33 The flask was charged with cyclopentadiene (295 grams, 4.46
34 mol) and benzene (1.4 L). The dienophile N-methylmaleimide

-28-

01 (30.1 grams, 0.45 mol) was added at room temperature
02 (exotherm noted), and the homogeneous yellow solution was
03 heated to reflux for 24 hours. Thin layer chromatography
04 (silica, 40% ethyl acetate/hexane) was used to monitor the
05 disappearance of maleimide. The reaction mixture was
06 concentrated by rotary evaporation to yield a mixture of oil
07 and solid products, which was taken up in 200 ml of CH_2Cl_2
08 and transferred to a separatory funnel. Water (200 ml) was
09 added and the pH of the aqueous layer adjusted to ≤ 1 using
10 conc. HCl. The phases were separated and the organic phase
11 was washed once more with H_2O (200 ml). After drying over
12 MgSO_4 , the organic phase was filtered and concentrated to
13 yield an oil and solid mixture which was recrystallized from
14 500 ml of hot Et_2O . The ethereal solution was placed in the
15 refrigerator overnight and the resulting white crystals of
16 the Diels-Alder imide were collected by vacuum filtration
17 and washed with a small amount of cold ether (65.43 grams,
18 82% yield, mp 103-105°C).

19

20 Reduction of Diels-Alder imide:

21

22 A 3-L, 3-necked flask was fitted with a mechanical stirrer,
23 addition funnel and reflux condenser. The Diels-Alder imide
24 (61.5 grams, 0.35 mol) was dissolved in 495 mL of CH_2Cl_2 in
25 the addition funnel. The flask was charged with LiAlH_4
26 (41.6 grams, 1.04 mol) and anhydrous Et_2O (990 mL) and the
27 system was placed under N_2 . The imide solution was added
28 slowly to the LiAlH_4 suspension. Gas evolution and an
29 exotherm were noted. Addition of the imide solution was
30 complete after approximately 1 hour and the grey
31 heterogeneous solution was allowed to stir under N_2
32 overnight. Thin layer chromatography (silica plates, 5%
33 MeOH/95% CH_2Cl_2) indicated the absence of starting material.

34

-29-

01 The reaction was carefully worked up in the following
02 manner: 38.5 mL of H₂O was added slowly to the reaction.
03 Vigorous gas evolution was noted as well as an exotherm.
04 This step was followed by the cautious addition of 38.5 mL
05 of 15% aqueous NaOH solution. Another 115 mL of H₂O was
06 added and the mixture, which turned from grey to white, was
07 stirred for 1 hour at room temperature. The solids were
08 removed by filtration and washed with CH₂Cl₂. The aqueous
09 layer was acidified with conc. HCl to pH ≤ 1 and the
10 non-basic organic impurities removed in the organic phase.
11 The aqueous layer was then made basic (pH ≤ 12) with 50%
12 NaOH and the crude tertiary amine was isolated by extracting
13 twice with CH₂Cl₂. The organic layers were combined and
14 dried over MgSO₄. Following filtration, the solution was
15 concentrated to yield 41.4 g (52%) of the amine, which was
16 taken directly to the next step. IR and ¹³C NMR spectroscopy
17 could be used to monitor the disappearance of the imide
18 functionality (1700 cm⁻¹ and 177.5 ppm, respectively).
19

20 Quaternization of the
21 4-Methyl-4-aza-tricyclo[5.2.1.0]dec-8-ene:
22

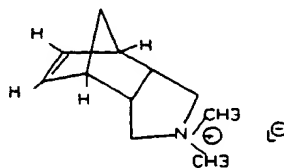
23 The amine (15.0 grams, 0.10 mol) was dissolved in 100 mL of
24 CHCl₃ in a 250-mL round-bottomed flask which was equipped
25 with an addition funnel and magnetic stirrer. The reaction
26 flask was immersed in an ice bath and the addition funnel
27 charged with CH₃I (28.7 grams, 0.20 mol). The CH₃I was added
28 to the amine over a 10-minute period (exothermic reaction)
29 and the homogeneous solution was stirred at room temperature
30 for 3 days. Diethyl ether (100 mL) was added to the
31 reaction mixture and the yellow solids were collected by
32 filtration and washed with more ether. These solids were
33 recrystallized from hot acetone/Et₂O (a small amount of MeOH
34

-30-

was added to aid in dissolution of solid) to afford 21.2 grams of an aza-polycyclic compound having an iodide anion. Bio-Rad AG1-X8 anion exchange resin was used to convert the iodide salt to the corresponding hydroxide form in 90.5% yield. The yield of the conversion was based upon titration of the resultant solution using phenolphthalein as the indicator.

The aza-polycyclic templating agent of Example 1 had the structure shown below.

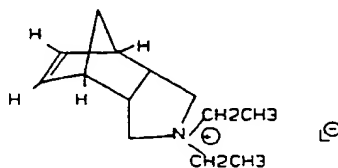
(VI)



Example 2

Example 1 was repeated, except N-ethylmaleimide was used as the dienophile and $\text{CH}_3\text{CH}_2\text{I}$ was used instead of CH_3I in the quaternization step. The resulting product had the structure of Structure VII below, with the alkyl groups surrounding the positively charged nitrogen being ethyl rather than methyl.

(VII)



31-

01

Example 3

02

03 Example 2 was repeated, except CH_3I was used in the
04 quaternization step, giving a cationic templating agent
05 Structure VIII.

06

07

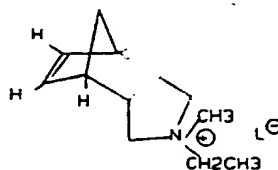
08

(VIII)

10

11

12



13

Example 4

14

15 Example 1 was repeated, except spiro[2.4]hepta-4,6-diene was
16 used as the diene; AlCl_3 was used as a Lewis acid, and the
17 reaction was not heated. In the resulting Structure IX the
18 bridging carbon is part of a spirocyclic cyclopropyl group.

19

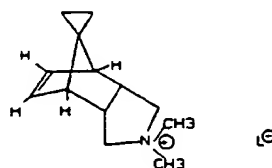
20

21

(IX)

23

24



25

Example 5

26

27 Example 4 was repeated, except N-ethylmaleimide was used as
28 the dienophile and $\text{CH}_3\text{CH}_2\text{I}$ was used instead of CH_3I in the
29 quaternization step, to give Structure X.

30

31

32

33

34

-32-

01

02

03

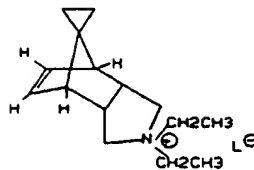
04 (X)

05

06

07

08

Example 6

09 Example 1 was repeated, except 1,3-cyclohexadiene was used
10 as the diene and toluene was used as the solvent. In the
11 resulting Structure XI the bridging radical has been
12 expanded from one to two carbon atoms.

13

14

15

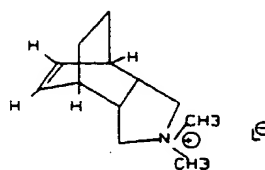
16 (XI)

17

18

19

20

Example 7

21 Example 6 was repeated, except N-ethylmaleimide was used as
22 the dienophile and CH₃CH₂I was used instead of CH₃I in the
23 quaternization step to give Structure XII.

24

25

26

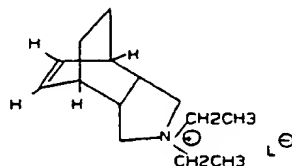
27 (XII)

28

29

30

31

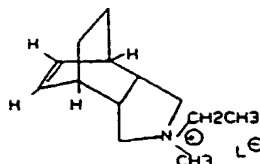
Example 8

32 Example 7 was repeated, except CH₃I was used in the
33 quaternization step to give Structure XIII.

34

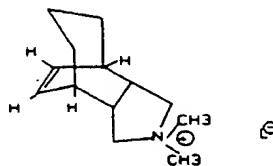
-33-

(XIII)

Example 9

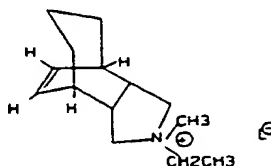
Example 6 was repeated, except 1-3,cycloheptadiene was used as the diene, and the reaction was heated for four (4) days to give Structure XIV.

(XIV)

Example 10

Example 9 was repeated, except CH₃CH₂I was used instead of CH₃I in the quaternization step to give Structure XV.

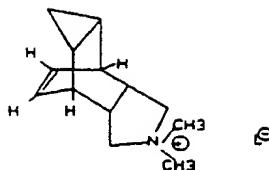
(XV)

Example 11

Example 6 was repeated, except cycloheptatriene was used as the diene to give Structure XVI.

-34-

(XVI)



Examples 12-20 illustrate using templates of this invention under a variety of inorganic conditions to obtain crystalline products. These non-limiting examples illustrate preferred conditions of the invention.

It can be seen that one of the desirable features of this invention is that a wide variety of crystalline products can be prepared. As is the case in most molecular sieve syntheses, a given template may not necessarily produce a crystalline product or a single molecular sieve over all inorganic composition ranges.

Example 12: ALPO reaction

4.05 Grams of Catapal B (alumina source) were added with stirring to 6.84 grams of an 86% H_3PO_4 solution over a 1-hour period. An additional 1 gram of water was added to aid in stirring, which was continued for 3 hours after the Catapal addition was complete. 1.81 Grams of this stock solution was transferred to a Teflon cup of a Parr 4745 reactor. A stir bar was added and 4.45 grams of a 0.56 M solution of the template of Example 7 as the hydroxide salt was added while stirring. The resultant thick white gel was stirred overnight at room temperature. The reactor was then heated to 150°C in a Blue M oven. After 48 hours, an increase in pH was noted and a settled product was obtained. The solids were filtered, washed with water, dried and determined by XRD to be ALPO-5.

-35-

01 Example 13: ALPO reaction

02

03 The procedure of Example 12 was repeated, except that
04 3.41 grams of a 0.73 M solution of the template from
05 Example 2 as the hydroxide salt was used. After two days,
06 the product isolated was ALPO-5.

07

08 Example 14: ALPO reaction

09

10 The procedure of Example 12 was repeated, except that
11 4.05 grams of a 0.62 M solution of the template from
12 Example 6 as the hydroxide salt was used. The product
13 isolated was ALPO-5.

14

15 Example 15: ALPO reaction

16

17 The procedure of Example 12 was repeated, except that
18 4.19 grams of a 0.59 M solution of the template from
19 Example 10 as the hydroxide salt was used. The product
20 isolated was ALPO-5.

21

22 Example 16: SAPO reaction

23

24 4.04 Grams of Catapal B were added with stirring to a
25 mixture of 6.83 grams of an 86% H_3PO_4 solution and
26 10.00 grams of water over a period of one hour. The
27 resulting gel was aged for one hour, after which was added
28 0.37 grams of Cabosil M-5 fumed silica. 2.9 Grams of the
29 resulting solution was transferred to a Teflon cup of a Parr
30 4745 reactor, and 3.41 grams of a 0.734 M solution of the
31 template from Example 2 (structure VII) was slowly added
32 with stirring. The resulting reaction mixture was heated at
33 150°C for 48 hours, after which a settled product was
34 obtained. The solids were filtered, washed with water,

-36-

01 dried and determined by XRD to be SAPO-5 with a small amount
02 of SAPO-34.

03

04

Example 17: SAPO reaction

05

06 The same reaction mixture as described in Example 16 was
07 prepared, with the exception that the mixture was heated at
08 170°C for 48 hours. The products from this reaction were
09 determined by XRD to be SAPO-5 with a small amount of
10 SAPO-34.

11

12

Example 18: SAPO reaction

13

14 The same reaction mixture as described in Example 16 was
15 prepared, with the exception that 4.29 grams of a 0.58 M
16 solution of the template prepared in Example 6
17 (structure XI) as the hydroxide salt was used instead of the
18 template from Example 2. After heating for 48 hours at
19 150°C, a settled product was obtained and determined by XRD
20 to be SAPO-5 with a trace amount of SAPO-34.

21

22

Example 19: SAPO reaction

23

24 The same reaction mixture as described in Example 16 was
25 prepared, with the exception that 4.45 grams of a 0.56 M
26 solution of the template prepared in Example 7
27 (structure XII) as the hydroxide salt was used instead of
28 the template from Example 2. After heating for 48 hours at
29 150°C, a settled product was obtained and determined by XRD
30 to be SAPO-5.

31

32

33

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-37-

01 Example 20: SAPO reaction

02

03 The same reaction mixture as described in Example 16 was
04 prepared, with the exception that 3.83 grams of a 0.65 M
05 solution of the template prepared in Example 1 (structure
06 VI) as the hydroxide salt was used instead of the template
07 from Example 2. After heating for 48 hours at 150°C, a
08 settled product was obtained and determined by XRD to be a
09 mixture of SAPO-5 and SAPO-34.

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01 WHAT IS CLAIMED IS:

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03 1. A method for preparing a crystalline molecular sieve
 04 comprising oxides of one or more trivalent element(s)
 05 and oxides of one or more pentavalent element(s), said
 06 method comprising contacting under crystallization
 07 conditions one or more active sources of said oxides
 08 with a templating agent having a molecular structure of
 09 the form:

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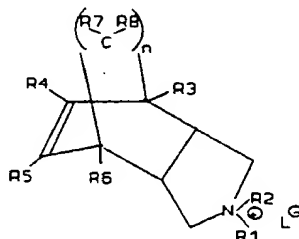
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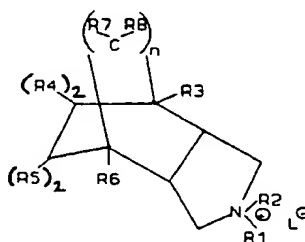
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(IA)



wherein:

R1 and R2 are at each independent occurrence
 selected from the group consisting of hydrogen, a
 lower alkyl group, and when taken together, a
 spirocyclic group having from 3 to 6 carbon atoms;

R3, R4, R5 and R6 are at each independent
 occurrence selected from the group consisting of
 hydrogen, halogen, and a lower alkyl group;

-39-

01 n has at each independent occurrence a value of 1,
02 2, 3, or 4;

03

04 R7 and R8 are at each independent occurrence
05 selected from the group consisting of hydrogen,
06 and a lower alkyl group, and when n is one (1), R7
07 and R8 can be taken together to form a spirocyclic
08 group having from 3 to 6 carbon atoms; and when n
09 is two (2) or greater, one of R7 and R8 on one
10 carbon atom can be taken together with one of R7
11 and R8 on an adjacent carbon atom to form a ring
12 having from 3 to 6 carbon atoms; and

13

14 L is an anion which is not detrimental to the
15 formation of the molecular sieve;

16

17 or a molecular structure of the form:

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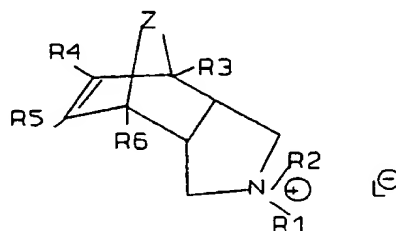
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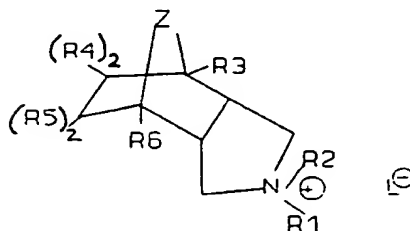
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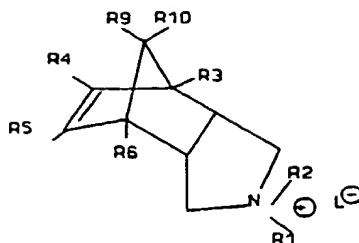
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-40-

- 01 wherein Z is at each independent occurrence selected
02 from the group consisting of oxygen, nitrogen, sulfur,
03 and a hydrocarbyl radical; and
04
05 R1, R2, R3, R4, R5, R6, and L are as defined above.
06
- 07 2. The method according to Claim 1 wherein R1 and R2 are
08 each selected from the group consisting of hydrogen, an
09 alkyl group having from 1 to 3 carbon atoms, and when
10 taken together, a spirocyclic group having from 4 to 5
11 carbon atoms.
12
- 13 3. The method according to Claim 1 wherein R3, R4, R5 and
14 R6 are each selected from the group consisting of
15 hydrogen and an alkyl group having from 1 to 3 carbon
16 atoms.
17
- 18 4. The method according to Claim 1 wherein R7 and R8 are
19 each selected from the group consisting of hydrogen,
20 and an alkyl group having from 1 to 3 carbon atoms, and
21 when n is one (1), R7 and R8 can be taken together to
22 form a spirocyclic group having from 3 to 6 carbon
23 atoms; and when n is two (2) or greater, one of R7 and
24 R8 on one carbon atom can be taken together with one of
25 R7 and R8 on an adjacent carbon atom to form a ring
26 having from 3 to 6 carbon atoms.
27
- 28 5. The method according to Claim 1 wherein the templating
29 agent has a molecular structure of the form:
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-41-



wherein:

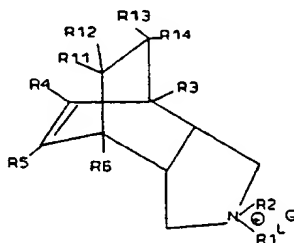
R1, R2, R3, R4, R5, R6 and L are as defined in Claim 1; and

R9 and R10 are each selected from the group consisting of hydrogen, a lower alkyl group, and when taken together, a spirocyclic group having from 3 to 6 carbon atoms.

6. The method according to Claim 5 wherein R1 and R2 are selected from the group consisting of hydrogen, an alkyl group having from 1 to 3 carbon atoms, and when taken together, a spirocyclic group having from 4 to 5 carbon atoms.
7. The method according to Claim 5 wherein R3, R4, R5 and R6 are each selected from the group consisting of hydrogen and an alkyl group having from 1 to 3 carbon atoms.
8. The method according to Claim 5 wherein R9 and R10 are each selected from the group consisting of hydrogen, an alkyl group having from 1 to 3 carbon atoms, and when taken together, a spirocyclic group having from 3 to 6 carbon atoms.

-42-

- 01 9. The method according to Claim 5 wherein R3, R4, R5, R6,
02 R9, and R10 are the same and each is hydrogen.
03
- 04 10. The method of Claim 9 wherein R1 and R2 are the same
05 and each is methyl.
06
- 07 11. The method according to Claim 9 wherein R1 is methyl,
08 R2 is ethyl.
09
- 10 12. The method according to Claim 9 wherein R1 and R2 are
11 the same and each is ethyl.
12
- 13 13. The method according to Claim 5 wherein R1 and R2 are
14 the same and each is methyl, and R3, R4, R5, and R6,
15 are the same and each is hydrogen, and R9 and R10 are
16 taken together to form a spirocyclic cyclopropane ring.
17
- 18 14. The method according to Claim 13 wherein R1 and R2 are
19 the same and each is ethyl.
20
- 21 15. The method according to Claim 1 wherein the templating
22 agent has a molecular structure of the form:
23
24



31 wherein:

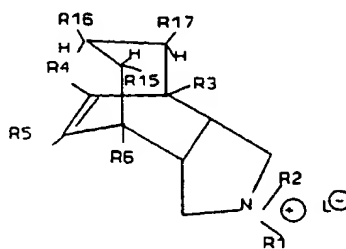
32
33 R1, R2, R3, R4, R5, R6 and L are as defined in
34 Claim 1; and

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- 01 R11, R12, R13, and R14 are each selected from the
02 group consisting of hydrogen, and a lower alkyl
03 group.
04
- 05 16. The method according to Claim 15 wherein R1 and R2 are
06 selected from the group consisting of hydrogen, an
07 alkyl group having from 1 to 3 carbon atoms, and when
08 taken together, a spirocyclic group having from 4 to 5
09 carbon atoms.
10
- 11 17. The method according to Claim 15 wherein R3, R4, R5 and
12 R6 are each selected from the group consisting of
13 hydrogen and an alkyl group having from 1 to 3 carbon
14 atoms.
15
- 16 18. The method according to Claim 15 wherein R11, R12, R13,
17 and R14 are each selected from the group consisting of
18 hydrogen, and an alkyl group having from 1 to 3 carbon
19 atoms.
20
- 21 19. The method according to Claim 15 wherein R3, R4, R5,
22 and R6 are the same and each is hydrogen.
23
- 24 20. The method according to Claim 19 wherein R11, R12, R13,
25 and R14 are the same and each is hydrogen.
26
- 27 21. The method according to Claim 20 wherein R1 and R2 are
28 the same and each is methyl.
29
- 30 22. The method according to Claim 20 wherein R1 is methyl
31 and R2 is ethyl.
32
- 33 23. The method according to Claim 20 wherein R1 and R2 are
34 the same and each is ethyl.

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- 01 24. The method according to Claim 1 wherein the templating
02 agent has a molecular structure of the form:



12 wherein:

13 R1, R2, R3, R4, R5, R6 and L are as defined in
14 Claim 1; and

15 R15, R16, and R17 are each selected from the group
16 consisting of hydrogen, and a lower alkyl group.
17

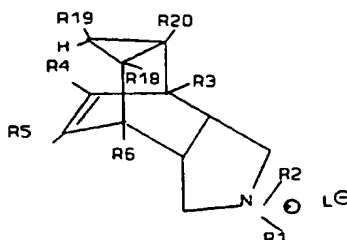
- 18 25. The method according to Claim 24 wherein R1 and R2 are
19 selected from the group consisting of hydrogen, an
20 alkyl group having from 1 to 3 carbon atoms, and when
21 taken together, a spirocyclic group having from 4 to 5
22 carbon atoms.

- 23
24 26. The method according to Claim 24 wherein R3, R4, R5 and
25 R6 are each selected from the group consisting of
26 hydrogen and an alkyl group having from 1 to 3 carbon
27 atoms.

- 28
29 27. The method according to Claim 24 wherein R15, R16, and
30 R17 are each selected from the group consisting of
31 hydrogen, and an alkyl group having from 1 to 3 carbon
32 atoms.
33
34

-45-

- 01 28. The method according to Claim 24 wherein R3, R4, R5,
02 and R6 are the same and each is hydrogen.
03
- 04 29. The method according to Claim 28 wherein R15, R16, and
05 R17 are the same and each is hydrogen.
06
- 07 30. The method according to Claim 29 wherein R1 and R2 are
08 the same and each is methyl.
09
- 10 31. The method according to Claim 29 wherein R1 is methyl
11 and R2 is ethyl.
12
- 13 32. The method according to Claim 1 wherein the templating
14 agent has a molecular structure of the form:
15



22
23 wherein:

24
25 R1, R2, R3, R4, R5, R6 and L are as defined in
26 Claim 1; and

27
28 R18, R19, and R20 are each selected from the group
29 consisting of hydrogen, and a lower alkyl group.

- 30
31 33. The method according to Claim 32 wherein R1 and R2 are
32 selected from the group consisting of hydrogen, an
33 alkyl group having from 1 to 3 carbon atoms, and when
34

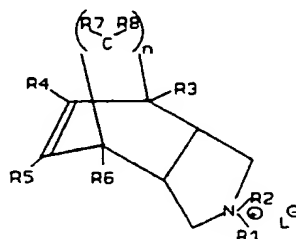
-46-

- 01 taken together, a spirocyclic group having from 4 to 5
02 carbon atoms.
03
- 04 34. The method according to Claim 32 wherein R3, R4, R5 and
05 R6 are each selected from the group consisting of
06 hydrogen and an alkyl group having from 1 to 3 carbon
07 atoms.
08
- 09 35. The method according to Claim 32 wherein R18, R19, and
10 R20 are each selected from the group consisting of
11 hydrogen, and an alkyl group having from 1 to 3 carbon
12 atoms.
13
- 14 36. The method according to Claim 32 wherein R3, R4, R5,
15 and R6 are the same and each is hydrogen.
16
- 17 37. The method according to Claim 36 wherein R18, R19, and
18 R20 are the same and each is hydrogen.
19
- 20 38. The method according to Claim 37 wherein R1 and R2 are
21 the same and each is methyl.
22
- 23 39. The method according to Claim 1 wherein L is selected
24 from the group consisting of fluoride, chloride,
25 bromide, iodide, hydroxide, acetate, sulfate, and
26 carboxylate.
27
- 28 40. The method according to Claim 39 wherein L is
29 hydroxide.
30
- 31 41. The method according to Claim 1 wherein the trivalent
32 element is aluminum.
33
34

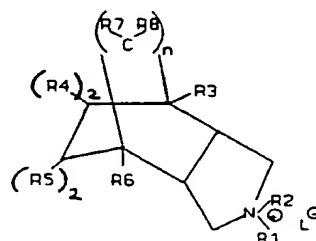
-47-

- 01 42. The method according to Claim 1 wherein the pentavalent
 02 element is phosphorous.
 03
- 04 43. The method according to Claim 1 wherein the crystalline
 05 molecular sieve further comprises an oxide of one or
 06 more tetravalent element(s).
 07
- 08 44. The method according to Claim 43 wherein the
 09 tetravalent element is silicon.
 10
- 11 45. A method for preparing a crystalline molecular sieve
 12 having a three-dimensional microporous framework
 13 structure comprising $[\text{AlO}_2]$ and $[\text{PO}_2]$ oxide units, said
 14 method comprising contacting sources of said oxide
 15 unites and a templating agent having a molecular
 16 structure of the form:
 17

(I)



(IA)



wherein:

-48-

01 R1 and R2 are at each independent occurrence
02 selected from the group consisting of hydrogen, a
03 lower alkyl group, and when taken together, a
04 spirocyclic group having from 3 to 6 carbon atoms;
05

06 R3, R4, R5 and R6 are at each independent
07 occurrence selected from the group consisting of
08 hydrogen, halogen, and a lower alkyl group;
09

10 n has at each independent occurrence a value of 1,
11 2, 3, or 4;
12

13 R7 and R8 are at each independent occurrence
14 selected from the group consisting of hydrogen,
15 and a lower alkyl group, and when n is one (1), R7
16 and R8 can be taken together to form a spirocyclic
17 group having from 3 to 6 carbon atoms; and when n
18 is two (2) or greater, one of R7 and R8 on one
19 carbon atom can be taken together with one of R7
20 and R8 on an adjacent carbon atom to form a ring
21 having from 3 to 6 carbon atoms; and
22

23 L is an anion which is not detrimental to the
24 formation of the molecular sieve;

25 or a molecular structure of the form:
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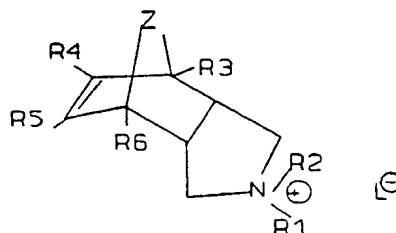
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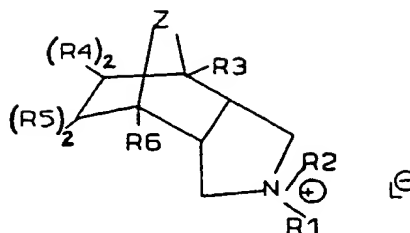
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wherein Z is at each independent occurrence selected from the group consisting of oxygen, nitrogen, sulfur, and an alkylene radical; and

R1, R2, R3, R4, R5, R6, and L are as defined above.

46. The method according to Claim 45 wherein the framework structure further comprises an oxide of at least one element other than aluminum and phosphorous which is capable of forming an oxide in tetrahedral coordination with $[AlO_2]$ and $[PO_2]$ oxide structural units in a crystalline molecular sieve.
47. The method according to Claim 46 wherein the element other than aluminum and phosphorous is selected from the group consisting of arsenic, beryllium, boron, chromium, cobalt, gallium, germanium, iron, lithium, magnesium, manganese, silicon, titanium, vanadium, and zinc.
48. The method according to Claim 46 wherein the element is selected from the group consisting of silicon, magnesium, manganese, cobalt, and zinc.
49. The method according to Claim 46 wherein the element is silicon.

-50-

01 50. The method according to Claim 45 wherein the molecular
02 sieve is $\text{AlPO}_4\text{-5}$.

03

04 51. A crystalline molecular sieve comprising oxides of one
05 or more trivalent element(s) and of one or more
06 pentavalent element(s), and having therein the
07 templating agent of Claim 1.

08

09 52. The crystalline molecular sieve of Claim 51 having a
10 molar composition, as synthesized and in the anhydrous
11 state, as follows:

12

13



14

15 wherein:

16

17

Q is the templating agent;

18

19

a has a value in the range of greater than zero
20 and no greater than about 0.3;

21

22

M is one or more elements capable of forming
23 stable M--O--P, M--O--Al, or M--O--M bonds in
24 crystalline oxide structures;

25

26

y and z each have a value of at least 0.01; and

27

28

the sum of x, y, and z is 1.

29

30 53. The composition according to Claim 52 wherein x has a
31 value equal to zero.

32

33 54. The composition according to Claim 52 wherein element M
34 is selected from the group consisting of arsenic,

-51-

- 01 beryllium, boron, chromium, cobalt, gallium, germanium,
02 iron, lithium, magnesium, manganese, silicon, titanium,
03 vanadium, and zinc.
04
- 05 55. The composition according to Claim 54 wherein element M
06 is selected from the group consisting of magnesium,
07 manganese, cobalt, and zinc.
08
- 09 56. The composition according to Claim 55 wherein element M
10 is silicon.
11
- 12 57. The process of thermally treating the crystalline
13 molecular sieve of Claim 51 at a temperature of about
14 200°C to about 800°C.
15
- 16 58. The process of thermally treating the crystalline
17 molecular sieve of Claim 52 at a temperature of about
18 200°C to about 800°C.
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/01402**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : C01B 37/04, 37/06

US CL : 423/706, 708, Dig 30; 502/208, 214

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/706, 708, Dig 30; 502/208, 214

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,A	US, A, 5,340,563 (Zones et al.) 23 August 1994.	
A	US, A, 5,281,407 (Nakagawa) 25 January 1994.	
A	US, A, 5,268,161 (Nakagawa) 7 December 1993.	
A	US, A, 5,254,514 (Nakagawa) 19 October 1993.	
A	US, A, 5,225,179 (Zones et al.) 6 July 1993.	
A	US, A, 4,793,984 (Lok et al.) 27 December 1988.	
A	US, A, 4,440,871 (Lok et al.) 3 April 1984.	

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

04 MARCH 1995

Date of mailing of the international search report

12 APR 1995

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

Mark Bell

Telephone No. (703) 305-0661

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